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TEMPERATURE DEPENDENCE OF X-RAY-INDUCED PHOTOCONDUCTIVITY IN KAPTON AND TEFLON*

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Introduction

Radiation-induced conductivity in dielectric materials is usually described by models in which the number of charge carriers is controlled by the kinetics of charge generation, recombination, and trapping. The fitting of experimental data to such models is highly speculative, since many of the parameters in the models can only be guessed. In particular the thermal energy required to release a trapped charge carrier is an important quantity in these models. A study of the temperature dependence of photoconductivity in dielectric materials can provide an estimate of the depth of trapping centers below the conduction level and can provide useful insights into carrier generation and removal processes during the delayed portion of the photoconductivity signal.

We have measured the X-ray-induced photoconductivity in Kapton (Dupont polyimide) and Teflon over the temperature range 100-500°K. The observed temperature dependence of the photoconductivity was strikingly different for these two materials. The qualitative behavior of the Kapton samples was consistent with the predictions of a model where the delayed photoconductivity signal is due to thermal release of trapped charge. In the case of the Teflon samples, the observed prompt conductivity was almost temperature independent and we observed a pronounced peak in the delayed component of the photoconductivity at about 360°K. The decay time of the delayed photoconductivity for Teflon was also observed to be temperature dependent. We discuss changes in the occupation of deep trapping levels as a possible mechanism for the observed thermal quenching of the Teflon photoconductivity.

Experimental Procedure

The method of making the measurements was similar to that used in earlier work[1], except that the present apparatus permits the sample temperature to be varied over the range 100-500°K. The samples were heated or cooled by blowing heated or cooled N_2 gas over them. The gas was pumped out before the measurements were made and the heat capacity of the sample chamber maintained the sample at a constant temperature while the measurements were made. The inner sample chamber was enclosed in another evacuated chamber, which thermally isolated the inner chamber and gave an additional degree of shielding against electrical noise.

The X-ray source was a Blumlein generator. The x-ray pulse was approximately 40 nsec FWHM in duration, resulting in a dose of 270 rads (air) at the sample position. The X-ray spectrum consisted of characteristic X-ray L lines from the tungsten anode superimposed on a bremsstrahlung spectrum. The peak dose rate was 4.7×10^9 rad/sec in Kapton and 9.5×10^9 rad/sec in Teflon.

The dielectric samples were made from commercially obtained films of Kapton and Teflon. Electrical contact was made by evaporating 1000Å thick aluminum electrodes onto the samples. The aluminum electrodes were backed by beryllium electrodes. The samples were 0.051 mm in thickness and the irradiated area was 5.6 cm^2. All surfaces within the sample chamber which were exposed to the X-ray beam were made of beryllium, to minimize charge transfer between the sample and its surroundings.

Results and Discussion

In an earlier paper[1] we considered a trapping model where electrons were excited into a conducting state at a rate $g(t)$, were captured into a shallow trapping level with a rate constant α_1, re-emitted into the conducting state with a rate constant α_2, and trapped into a recombination level with a rate constant α_3. We assumed that the carriers were not re-emitted from the deep level during the time span of the measurement. The charge carrier kinetics for this model are described by the equations

$$dn_c/dt = g(t) - \alpha_1 n_c(N_t - n_t) + \alpha_2 n_t(N_c - n_c) - \alpha_3 n_c(N_r - n_r) \tag{1}$$

$$dn_t/dt = \alpha_1 n_c(N_t - n_t) - \alpha_2 n_t(N_c - n_c), \tag{2}$$

where N_t is the density of shallow trapping levels, n_c is the density of conduction electrons, n_t is the density of trapped electrons, N_r is the density of recombination centers, n_r is the number of recombination centers occupied by electrons, and N_c is the density of conducting states. We assume that the holes produced by the irradiation are immobile.

One of the important parameters in any photoconductivity model is the generation rate of charge carriers. Photoconductivity in insulators is generally characterized by unusually large values of E_p, the absorbed energy per free-carrier pair. E_p values for insulators up to 10^4 eV per ion pair have been reported.[2] The unusually large values of E_p have been explained by some investigators in terms of geminate recombination.[3] Hughes[4] has shown geminate recombination to be the dominant recombination mechanism in poly-N-vinylcarbazole. The probability that an electron and hole will escape from each other before recombining can be computed from the theory of Onsager[5], and at low electric fields the escape probability, P, is described by

$$P = \exp(-e^2/\epsilon kTr_0)(1 + e^3E/2\epsilon k^2T^2) \tag{3}$$

where e is the electronic charge, ϵ is the dielectric constant, k is the Boltzmann constant, T is the absolute temperature, E is the electric field and r_0 is the initial separation of an electron-hole pair. At room temperature

and below we observe a linear dependence of peak photocurrent on electric field for both Kapton and Teflon. If geminate recombination controls the carrier generation, our data should be in the low-field regime where Eq. (3) applies. Since we observe only a slight temperature dependence for Teflon peak conductivity and essentially no temperature dependence for Kapton peak conductivity below room temperature, we conclude that during the time scale of our measurements geminate recombination is not important in the charge generation process.

Kapton:

The transient photoconductivity which is observed during and after pulsed irradiation consists of two components: the prompt conductivity, which occurs during the exciting pulse; and the delayed conductivity, which persists after the exciting pulse has ended. As the temperature is increased, the delayed conductivity of Kapton increases rapidly, but the decay time is relatively independent of temperature, as shown in Figure 1. Below room temperature the delayed conductivity is negligible. The delayed conductivity signal varies exponentially with the reciprocal of temperature, as shown in Figure 2. If the delayed carriers are generated as a result of thermal emission from traps, the data of Figure 2 indicate an activation energy (trap depth) of 0.36 eV. The increase of the prompt conductivity, which is observed above room temperature, appears to be due to the buildup of the delayed conductivity during the radiation pulse. Below room temperature the prompt conductivity is temperature independent.

Some of the parameters in Equations (1) and (2) can be estimated from our experimental data and from the work of other investigators. The mobility, μ, of the charge carriers is an important quantity, since we can compute the carrier concentration from the measured conductivity if we know the mobility. No measurements of mobility have been reported for Kapton, however, Hughes[6] found the "intrinsic" mobility of charge carriers in Mylar films to be about $2 \times 10^{-3} cm^2/v$-s. At room temperature the peak conductivity of Kapton is $5.5 \times 10^{-10} (ohm-cm)^{-1}$, so if we assume that the carrier mobility in Kapton is the same as Hughes measured in Mylar we obtain a peak carrier concentration of about $2 \times 10^{12} cm^{-3}$. We chose the generation rate, g, to be a Gaussian function of 40 nsec FWHM normalized to a total excitation of $10^{14} cm^{-3}$. This corresponds to an absorbed energy of 160 eV per electron-hole pair.

Our assumed value of mobility puts an upper limit on the values of α_1 and α_3, since the Langevin theory[7] places an upper limit of $4\pi e\mu/\varepsilon$ on diffusion-controlled rate constants. We assume that α_1 and α_3 have the largest values consistent with the Langevin theory, i.e., $\alpha_1 = \alpha_3 = 10^{-9} cm^3 s^{-1}$.

In thermal equilibrium the rates of capture and emission from the trapping level must be equal, leading to the equation

$$\alpha_2 = \alpha_1 (N_t/N_c) \exp(-b/kT) \qquad (4)$$

where b is the depth of the trapping level below the conduction level. From the temperature dependence of the Kapton delayed conductivity we estimate a trap depth of 0.36 eV. We estimate the trap density, N_t, to be $10^{18} cm^{-3}$, the

density of unoccupied recombination levels, $N_r - n_r$, to be $10^{16} cm^{-3}$ and the density of conducting states at room temperature to be $5 \times 10^{19} c^{-3}$, so from Equation (4) we obtain $2 \times 10^{-15} cm^3 s^{-1}$ and $10^{-17} cm^3 s^{-1}$ as the value of α_2 at $500°K$ and $300°K$, respectively. The values of α_2 computed using Equation (4) were much too small to give an appreciable delayed conductivity. In order to generate curves which qualitatively look like the experimental data we had to choose values of α_2 in the range $10^{-12} - 10^{-14} cm^3 s^{-1}$.

Numerical integration of Equations (1) and (2), using the assumed values of the coefficients gives the curves shown in Figure 3. The calculated curves show good qualitative agreement with the data of Figure 1, particularly in their temperature dependence.

The discrepancy between the calculated values of α_2 and the values of α_2 we used to fit the data does not appear to be strongly dependent of the choice of any of the parameters except α_1, and N_t. Since we can estimate the trap depth from our experimental data, we do not regard b as an adjustable parameter. When we tried to increase the calculated value of α_2 by increasing $\alpha_1 N_t$, we found that the trapping became so strong that the number of carriers became much too small to account for the delayed conductivity unless we assume a much larger mobility.

Although we cannot discount the possibility that we have made a poor choice of coefficients to quantitatively fit the data, the discrepancy may be of a more fundamental nature. One possibility is that the trapping level may be filled directly, rather than by capturing carriers from the conduction level. For example, the trapping level might represent an excited molecular state with dissociation as a possible mode of decay. In the event that there are other means of filling the trapping level than by capture of free carriers, Equation 4 does not apply and the value of α_2 need not be constrained by the value of $\alpha_1 N_t$.

Teflon:

The temperature dependence of the Teflon photoconductivity differs strikingly from that observed in Kapton. The photoconductivity signals from Teflon are shown in Figures 4 and 5. The prompt conductivity is almost independent of temperature and the delayed conductivity increases with temperature to about $360°K$ and then decreases with increasing temperature.

The observed temperature insensitivity of the peak conductivity in Teflon is probably due to the relative sizes of the delayed and prompt components. The magnitude of the delayed conductivity never rises above the peak room temperature photoconductivity (Figures 4 and 5) so that the delayed part never contributes very much to the peak component. This behavior is to be contrasted to that observed in Kapton (Figure 1) where the delayed conductivity at elevated temperatures is much larger than the room temperature peak component so that substantial contributions to the peak conductivity do occur.

The thermal quenching of the Teflon photoconductivity at elevated temperatures probably arises from temperature-induced changes in the occupation of trapping levels. A model for thermal quenching in a photoconductor has been proposed by Bube[8] where he considers a photoconductor containing a

recombination center with relatively large capture cross sections 'or both electrons and holes, and a sensitizing center which has a very small capture cross section for electrons and a much larger capture cross section for holes (for n-type sensitization). At sufficiently low temperatures or high excitation intensities, holes tend to build up preferentially in the sensitizing centers, thus increasing the electron lifetime and the photoconductivity. As the temperature is increased, fewer holes occupy the sensitizing centers and more holes reside in the recombination centers, thus decreasing the electron lifetime and quenching the photoconductivity. The model proposed by Bube is not directly applicable to our experimental results, however, because it is a steady state model.

In our experiments the density of carriers produced by the X-ray pulse ($10^{14} cm^{-3}$) was very small compared to the estimated trap densities ($10^{16} - 10^{18} cm^{-3}$), so the occupation of the trapping levels would be determined primarily by thermal equilibrium considerations. Under these conditions we look to changes in the equilibrium occupation of the trapping levels to account for the thermal quenching of the photoconductivity. The charge carrier kinetics described in Equations (1) and (2) provide a possible explanation of the observed thermal quenching. The ratio, R, of the two trapping terms in Equation (1) is given by

$$R = \alpha_1(N_t - n_t)/\alpha_3(N_r - n_r) \simeq \alpha_1 N_t/\alpha_3(N_r - n_r) \tag{4}$$

where n_r and n_t are the equilibrium densities of electrons in the recombination level and the trapping level, respectively.

As the temperature varies, R will be dominated by the quantity $(N_r - n_r)$, since α_1 and α_2 will have similar temperature dependences. If the recombination level lies above the Fermi level, $N_r - n_r$ will decrease with increasing temperature and the rate of electron trapping into the recombination level will decrease. If the recombination level lies slightly below the Fermi level, however, the occupation of the level will decrease and the rate of electron trapping into the recombination level will increase with temperature proportional to

$$N_r - n_r = N_r \left(1 + \exp \frac{E_f - E_r}{kT}\right)^{-1}, \tag{5}$$

where E_f is the Fermi energy and E_r is the energy of the recombination level. A recombination level lying slightly below the Fermi level could account for the observed decrease in delayed conductivity with increasing temperature. At elevated temperatures a higher proportion of the free carriers produced by the exciting pulse would be trapped into the recombination level and there would be fewer carriers in the shallow traps available for re-emission into the conduction level.

-6-

REFERENCES

1. K. C. Weingart, R. H. Barlett, R. S. Lee, and W. Hofer, IEEE Trans. Nucl. Sci. NS-19, 15 (1972).

2. D. M. J. Compton, G. T. Cheney, and R. A. Poll, J. Appl. Phys., 26, 2434 (1965).

3. J. L. Azarewicz, et al., Report AD 737 312, Defense Documentation Center, Alexandria, Virginia (1972).

4. R. C. Hughes, IEEE Trans, Nucl. Sci. NS-18, 281 (1971).

5. L. Onsager, Phys. Rev. 54, 554 (1938).

6. R. C. Hughes, Proceedings of the Second International Conference on Electrophotography, Society of Photographic Scientists and Engineers, Washington, D.C., 1974.

7. H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Oxford Press, New York, 1952, Chapter X.

8. R. H. Bube, Electronic Properties of Crystalline Solids, Academic Press, New York, 1974, Chapter 12.

FIGURE CAPTIONS

Figure 1 – Kapton photoconductivity signal as a function of temperature. The data shown are from digitized oscilloscope traces. To convert the signal to conductivity in $(\Omega cm)^{-1}$, multiply by $4.6(10^{-8})$.
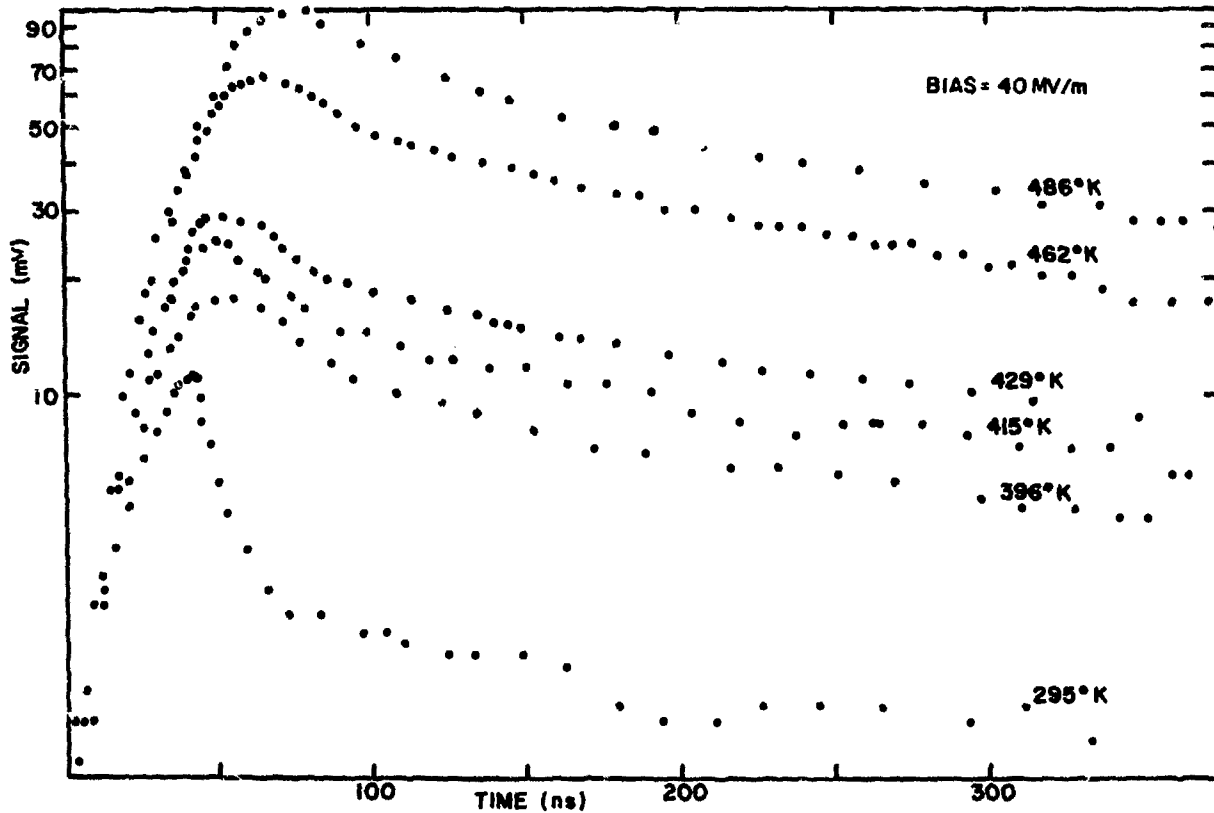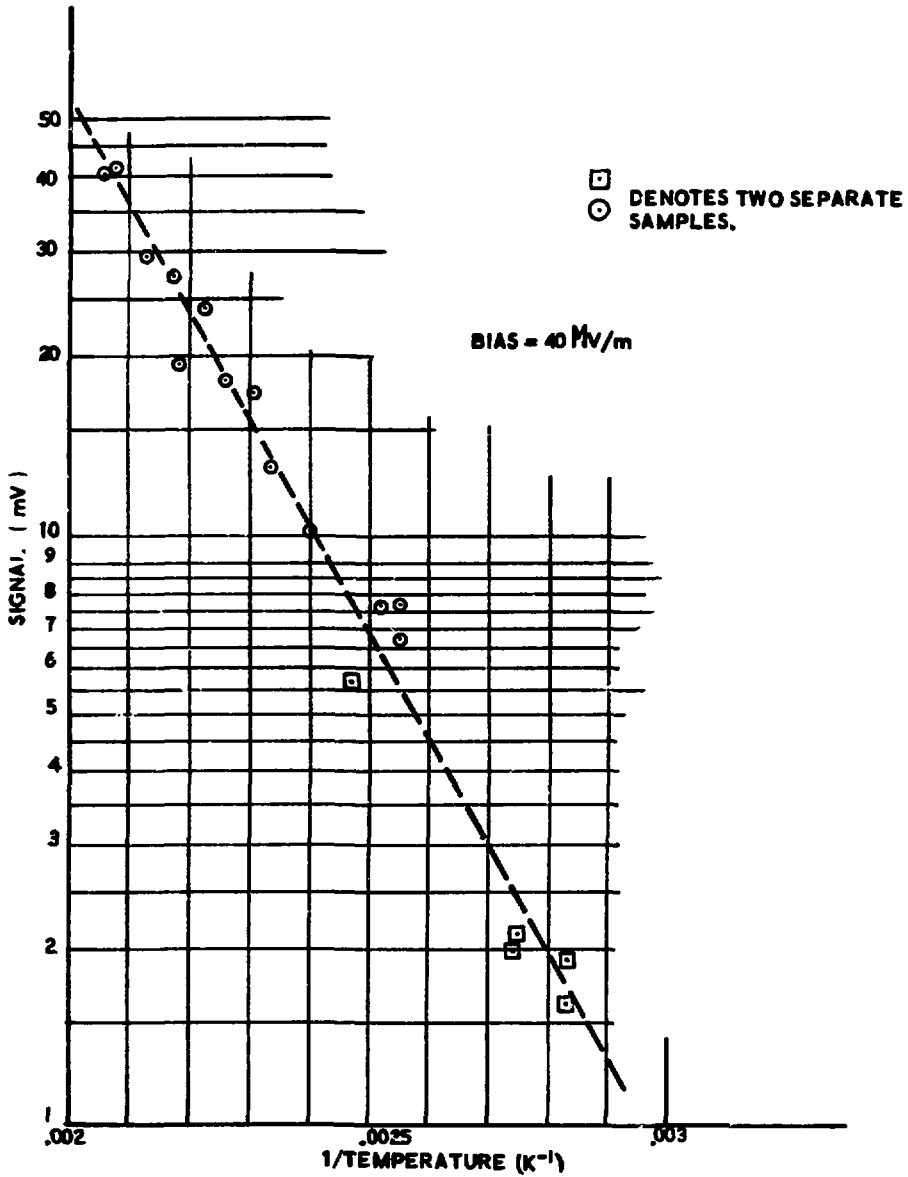
Figure 2 – Temperature dependence of the Kapton delayed conductivity signal. Plotted points are signal values (normalized to the same dose) 200 ns after the start of the exciting X-ray pulse.

Figure 3 – Dependence of free carrier density on temperature. The variation of the rate constant α_2 corresponds to a temperature variation from $300-500^\circ K$.

Figure 4 – Teflon photoconductivity signal at low temperatures. The data shown are from digitized oscilloscope traces. To convert the signal to conductivity in $(\Omega cm)^{-1}$, multiply by $2.8(10^{-8})$.

Figure 5 – Teflon photoconductivity signal at high tempreatures. The data shown are from digitized oscilloscope traces. To convert the signal to conductivity in $(\Omega cm)^{-1}$, multiply by $2.8(10^{-8})$.

FIGURE 1

FIGURE 2

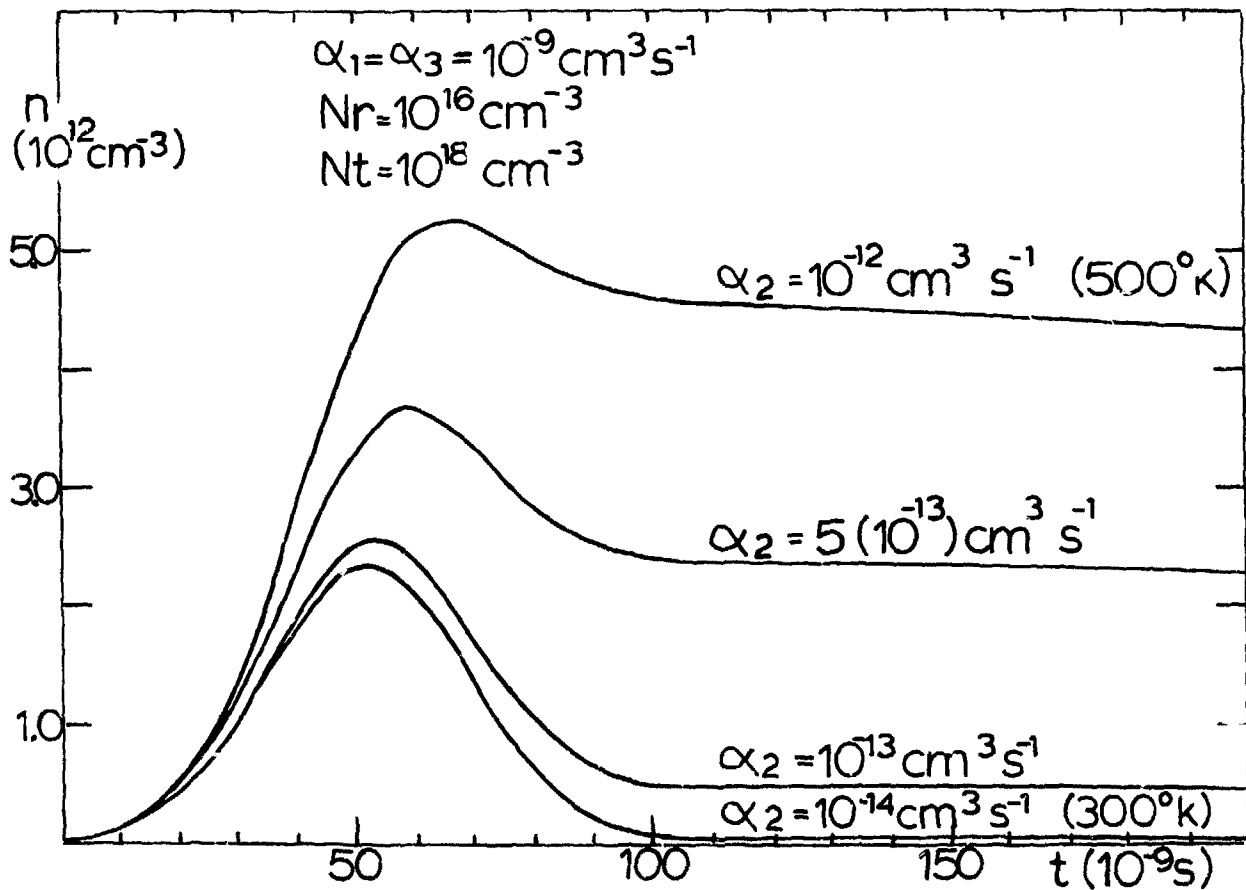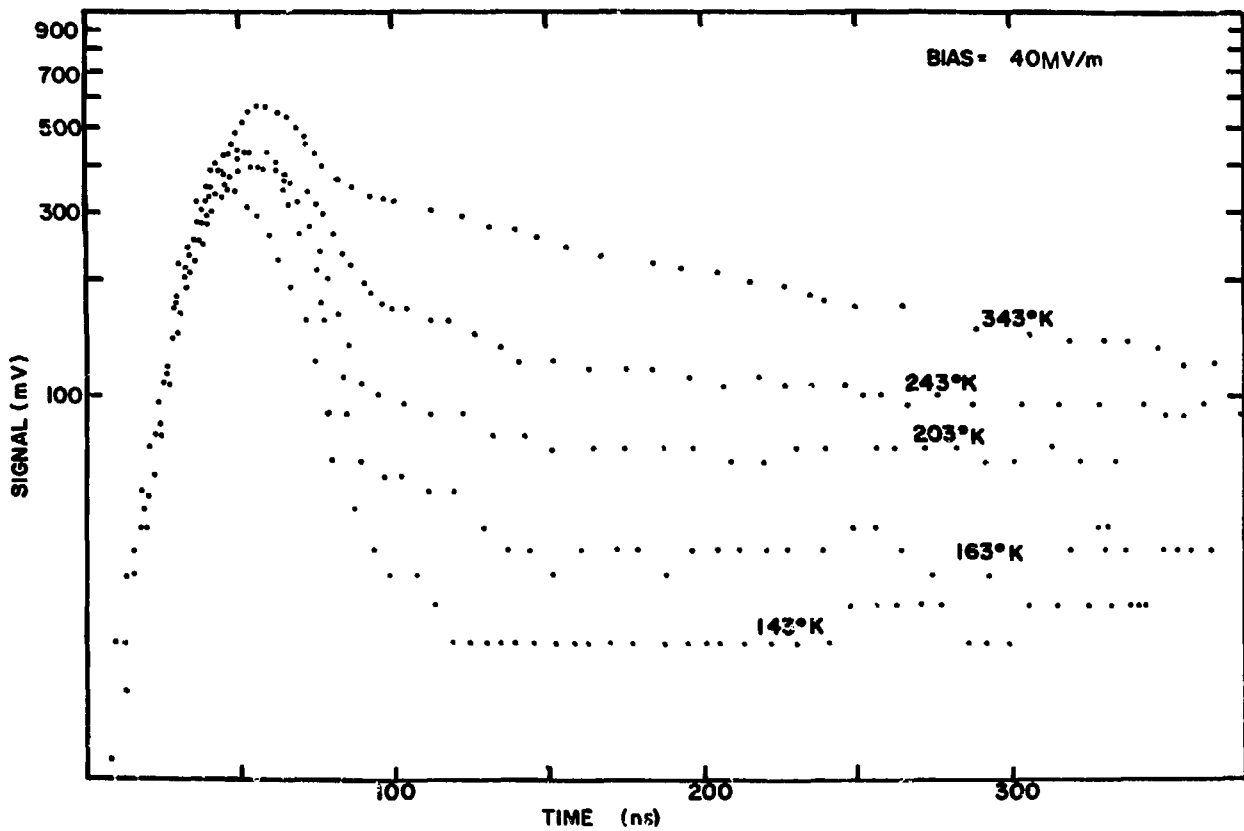$\alpha_1 = \alpha_3 = 10^{-9} cm^3 s^{-1}$

$Nr = 10^{16} cm^{-3}$

$Nt = 10^{18} cm^{-3}$

$\alpha_2 = 10^{-12} cm^3 s^{-1}$ (500°K)

$\alpha_2 = 5(10^{-13}) cm^3 s^{-1}$

$\alpha_2 = 10^{-13} cm^3 s^{-1}$

$\alpha_2 = 10^{-14} cm^3 s^{-1}$ (300°k)

n $(10^{12} cm^{-3})$

$t (10^{-9} s)$
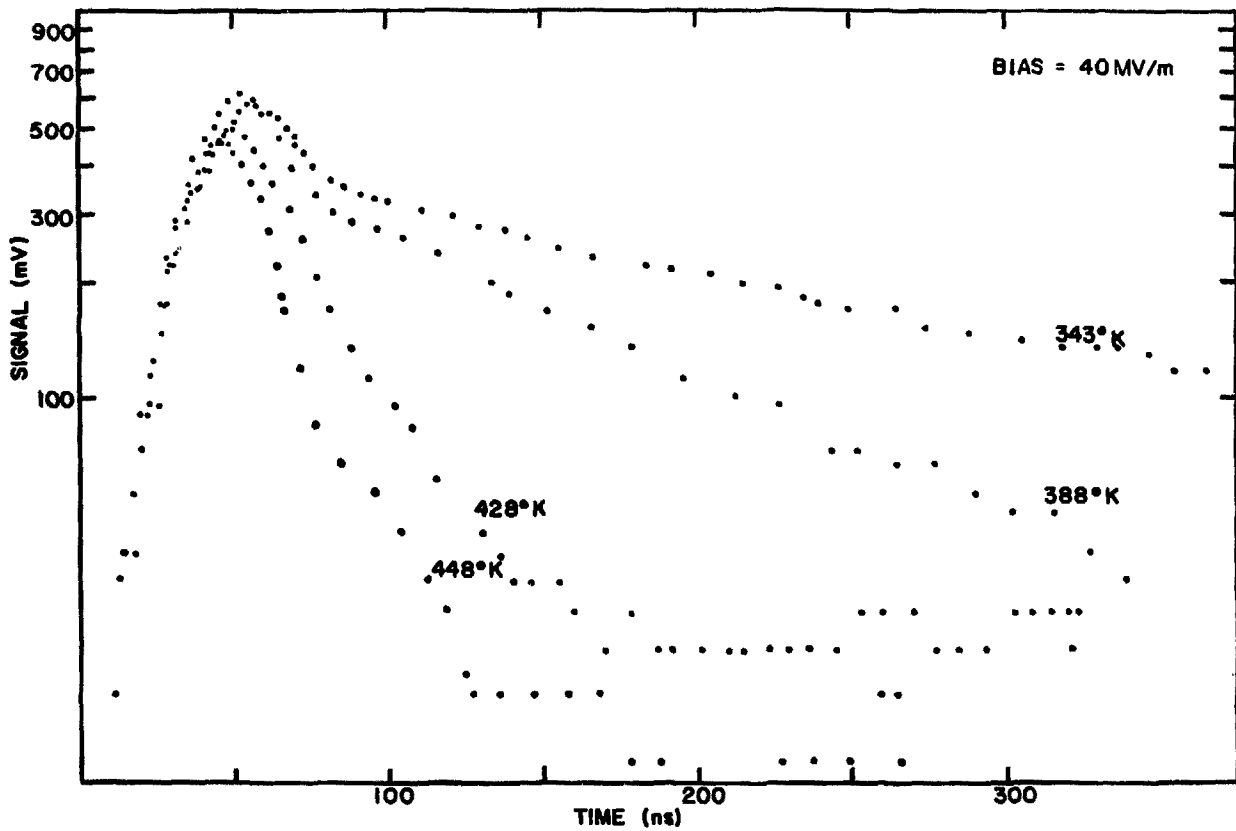
FIGURE 3

FIGURE 4

FIGURE 5

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